Pressurized Oxidative Recovery of Energy from Biomass

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Executive Summary

This study was conducted to evaluate the technical feasibility of using pressurized oxyfuel, the ThermoEnergy Integrated Power System (TIPS), to recover energy from biomass. The study was focused on two fronts—computer simulation of the TIPS plant and corrosion testing to determine the best materials of construction for the critical heat exchanger components of the process. The goals were to demonstrate that a successful strategy of applying the TIPS process to wood waste could be achieved.

To fully investigate the technical and economic benefits of using TIPS, it was necessary to model a conventional air-fired biomass power plant for comparison purposes. The TIPS process recovers and utilizes the latent heat of vaporization of water entrained in the fuel or produced during combustion. This latent heat energy is unavailable in the ambient processes.

An average composition of wood waste based on data from the Pacific Northwest, Pacific Southwest, and the South was used for the study. The high moisture content of wood waste is a major advantage of the TIPS process. The process can utilize the higher heating value of the fuel by condensing most of the water vapor in the flue gas and making the flue gas a useful source of heat. This is a considerable thermal efficiency gain over conventional power plants which use the lower heating value of the fuel.

The elevated pressure also allows TIPS the option of recovering CO_2 at near ambient temperatures with high purity oxygen used in combustion. Unlike ambient pressure processes which need high energy multi-stage CO_2 compression to supply pipeline quality product, TIPS is able to simply pump the CO_2 liquid using very little auxiliary power. In this study, a 15.0 MWe net biomass power plant was modeled, and when a CO_2 pump was included it only used 0.1 MWe auxiliary power. The need for refrigeration is eliminated at such pressures resulting in significant energy, capital, and operating and maintenance savings.

Since wood waste is a fuel with a high moisture and hydrogen content, it is one of the best applications for TIPS. The only way to fully utilize the latent heat is by using a pressurized system and the oxy-fuel approach allows for carbon capture and easier emission control. Pressurized operation also allows for easier emission control than atmospheric oxyfuel because presence of infiltration air in the atmospheric case. For the case of wood waste as the fuel however, the ability of TIPS to fully utilize the heat of condensation is the most valuable advantage of the process.

The project research showed that titanium alloys were the best materials of construction for the heat exchangers. All other materials tested failed to withstand even brief periods in the harsh environment (high temperature, acidic, and oxidizing conditions). Titanium was able to survive due to the formation of a stable TiO_2 passivation layer.

Introduction

A development program was undertaken by the University of Nevada, Reno (UNR) in conjunction with ThermoEnergy Power Systems, LLC (TEPS) to provide a preliminary design and process evaluation of a biomass fueled ThermoEnergy Integrated Power System (TIPS) process. TIPS is a patented process that uses oxygen instead of air for combustion (known as oxy-fuel combustion) at elevated pressure, thus eliminating nitrogen from the feed gas to the combustor and producing a highly enriched CO_2 stream ready for sequestration and industrial applications such as enhanced oil recovery (EOR) and coal bed methane (CBM) recovery[1]. ThermoEnergy provided the design basis and process modeling for this study while UNR conducted condensing heat exchanger materials corrosion and evaluation.

The TIPS process is different in many ways from atmospheric oxyfuel combustion. Operating at high pressure, the liquid-vapor equilibrium of the components in the combustion gas is shifted to allow for gas to liquid phase change. This leads to the water vapor in the flue gas condensing at higher temperatures creating heat at useful temperatures. This heat can be used for the boiler feed water (BFW), condensate return or for Combined Heat and Power (CHP) steam. Unlike conventional boilers operating at ambient pressure, TIPS almost fully utilizes the fuel's energy content. This makes TIPS much more efficient, as it uses the higher heating value (HHV) rather than the lower heating value (LHV). The high moisture content of biomass results in more of an advantage to the TIPS process. TIPS also has the potential to be more compact than conventional atmospheric combustion systems of similar capacity due to its compact size. Unlike other oxy-fuel designs, the TIPS relies on using compressors on the purified oxygen before combustion, rather than the multiple-stage compression of post-combustion gases in more conventional designs.

Another major advantage of TIPS is its ability to condense the CO_2 in the flue gas at ambient sink temperatures. In contrast, an oxyfuel process operating at ambient pressure requires the use of multi-staged compression along with interstage cooling, also called the product recovery train (PRT), for CO_2 capture and recovery at 2200 psi (NETL pipeline quality) [2]. The final PRT operating conditions are usually in the neighborhood of 28 bar and -60^{o}C so as to ensure high CO_2 capture rates with high product purity. This is an energy intensive process particularly because of its refrigeration requirements. The TIPS process is able to save significant capital, and operating and maintenance (O&M) costs due to the CO_2 capture at ambient temperatures [3].

Integrated emissions control is another key advantage to the TIPS process. It is known that for a typical coal-fired power plant, the emissions control capital and annual costs are about 25% and 38% of the total plant costs [4]. The TIPS process, operating at elevated pressure, can scrub particles out from the flue gas, and condense acid gases (SO_2 and SO_3) and mercury into the post-combustion stream. Hence, significant capital and annual savings can be achieved in this respect by using the TIPS process.

Computer simulation programs can be used to predict the thermodynamics, stream compositions and energy production of the TIPS process [5]. However, it is critical to the successful application of the process to find a suitable material for the critical heat exchangers that the process relies so heavily upon. It is precisely these two goals that were at the core of this R&D project—preparing an Aspen Plus model of the process, and deciding on the material of construction for the condensing heat exchanger.

Objectives

The specific objectives of this research project were as follows:

- Design Basis

  This included product/emission output requirements and constraints, fuel source, permitting requirements, and infrastructure requirements. Main focus was on the fuel source being an average of the wood waste compositions in the Pacific Northwest, Pacific Southwest, and Southern Regions.

- Process Modeling

  Based on the design parameters and configuration, a steady-state computer model was built to simulate the performance of a biomass-fueled TIPS process. The computer model consisted of all the major components of the boiler including the furnace, superheaters, reheaters, economizer, condensing heat exchanger and auxiliary parts.

- Materials Selection

  Process Modeling & design findings were combined with UNR's condensing heat exchanger materials and corrosion testing studies to complete a final report with all findings and recommendations for research and development.

This report represents the culmination of the studies as outlined herein. Because of the direct involvement of two individual investigative groups, the report is presented by activity: Part A is devoted to the Process Description and Modeling of the various biomass combustion approaches; Part B covers the laboratory study to find an effective material of construction for the heat exchangers of the process.

Part A: Process Description and Modeling

A1. Introduction

Biomass combustion to produce electricity is not a new concept. To best understand the output from any model, a direct comparison of results must be made. For this study, a

conventional 15 MW Biomass plant was used as the basis for comparison with oxy-fuel combustion.

The basis for the biomass composition was solidified with 9.9 trillion cubic feet of tree split data from Pacific Northwest regions (Western Washington, Puget Sound, and Olympic Peninsula), 20 trillion cubic feet from Pacific Southwest Regions (San Joaquin and Southern Resource Areas of California, North Interior Resource Area of California, and Eastern Oregon), and 110 trillion cubic feet from South Regions (Georgia, Kansas, and Central Florida). The averages from these regions were close enough that variability among trees is not considered a major factor. Table A1 shows how close the average wood composition from the Pacific Northwest, Pacific Southwest, and South were.

Table A1 Composition, HHV, and LHV Comparison of 3 Forest Regions in the U.S

Region	H_2O %	C %	H_2 %	O_2 %	N_2 %	S %	Ash %	HHV (Dry) kJ/kg	LHV (Dry) kJ/kg
Pacific Northwest	56.2	21.9	2.6	18.7	0.034	0.015	0.47	19690	18372
Pacific Southwest	53.7	23.7	2.8	18.6	0.34	0.0018	0.90	19986	18689
South	51.6	24.7	2.8	19.8	0.094	0.0015	0.94	19313	18013

The Pacific Southwest's proximate, ultimate, and sulfur analyses were used for the study. Table A2 details the analyses used in the model. The values for the proximate and ultimate analyses were as received and the sulfur analysis is on a dry basis. These values were input into Aspen Plus for use in the calculations.

Table A2 Analysis of Wood Waste Fuel Used in Model

Proximate Analysis		**Ultimate Analysis**		**Sulfur Analysis**	
Moisture	53.7	Moisture	53.7	Pyritic	0.14
Ash	0.9	Carbon	23.6	Sulfate	0.03
Volatile Matter	49.5	Hydrogen	2.79	Organic	0.63
Fixed Carbon	49.6	Nitrogen	0.301		
HHV, kJ/kg	19254	Chlorine	0		
		Sulfur	0.18		
		Ash	0.903		
		Oxygen	18.6		
All Values as-received		All Values as-received		All Values Dry Basis	

Using this data, a pressurized oxyfuel model operating at 800 psia was developed for both an oxyfuel plant and a plant using pressure swing adsorption where air was compressed to 35 psi and a 40% oxygen stream entered the furnace. A model for an ambient pressure conventional biomass plant was also developed as a base scenario with

the same general assumptions as the above mentioned plants. See Figures A1 – A11 for schematics for these cases.

The Peng-Robinson Equation of State[1] was used in this study, due to its accuracy at high pressures to calculate all thermodynamic properties for all fluids other than steam and water. The Peng-Robinson EOS is generally superior to the Soave equation in predicting the liquid densities of many materials, especially nonpolar ones. Properties of steam and water were computed using the American Society of Mechanical Engineering (ASME) and National Bureau of Standard (NBS) steam tables. Aspen Plus simulation software was used throughout this study.

A2. Baseline Conditions and Assumptions

A2.1 Fuel

An average of the Pacific Northwest, Pacific Southwest, and South Regions was selected for this study due to the low variance in all regions of the compositions, higher heating values, and low sulfur content. Wood waste is particularly advantageous to the TIPS process due to its high moisture content and low sulfur content. The ash softening temperature for wood waste is about 1020^{o}C. It is important to keep the furnace outlet temperature below the ash softening temperature if a dry ash combustor is employed.

A2.2 Air, Oxygen, and Ambient Conditions

The ambient conditions for this study were:

- Ambient Temperature was 60^{o}F.
- Ambient Pressure was 14.7 psia.

Table A3 Compositions of Oxidant Streams Entering Furnace

Air Composition	*Volume %*
Nitrogen	77.316
Oxygen	20.747

[1] Peng-Robinson equation of state

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45724 R^2 T_c^2}{P_c}$$

$$b = \frac{0.07780 RT_c}{P_c}$$

$$\alpha = \left(1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - T_r^{0.5}\right)\right)^2$$

$$T_r = \frac{T}{T_c}$$

Water	0.986
Argon	0.921
CO_2	0.03
Composition Exiting PSA	*Volume %*
Nitrogen	58.063
Oxygen	40.0
Water	0.986
Argon	0.921
CO_2	0.03
Assumed Composition Exiting ASU	*Volume %*
Oxygen	95
Argon	5

Table A3 shows the compositions of the oxidant streams used in the 3 cases modeled in this study. For the scope of this study, the air-separation unit (ASU) exit stream was assumed to be 95% Oxygen and 5% Argon. The pressure swing adsorption (PSA) exit composition was assumed to have 40% oxygen and this was a direct result of part of the nitrogen being separated from the main stream. Although this didn't lead to positive results, it was important to demonstrate the advantages of using oxyfuel. Oxygen purity has a significant impact on process energy requirements and the cost of CO_2 recovery.

A3. Conventional 15 MW Biomass Plant Model

A baseline model of a conventional 15 MW Biomass plant was developed for comparison with the pressurized oxyfuel and pressure swing adsorption models. The model was based on a typical fuel/air power plant using biomass as the fuel. It included a heat balance of the radiant and convective heat (superheater, evaporator, and economizer) between the flue gas and the boiler feed water/steam. The steam turbine was assumed to have a discharge pressure of 1 psia and an isentropic efficiency of 0.875. The steam in the Rankine Cycle entered the heat exchangers at 845 psia and had an 80 psia pressure drop. The only auxiliary power loss accounted for in this model was the boiler feed water (BFW) pump. This had a loss of 0.1 MW.

Although the only auxiliary loss in the model was the BFW Pump, there were other more important energy losses to consider. Because it operates at ambient pressure and is unable to fully utilize the latent heat of vaporization, about $1.84*10^7$ Btu/hr of heat was lost up the stack. Also, the flue gas heat loss up the stack amounted to $2.08 * 10^7$ Btu/hr. This energy could be used for producing additional steam allowing more power generation in the steam turbine. This energy is not recoverable in the conventional boiler. Figures A1 and A2 show the combustion cycle and the steam cycle used in the Aspen Plus model. Figure A2 is the same Rankine Cycle used in the PSA case as well as the pressurized oxyfuel case. The following is a list of abbreviations from Figures A1 – A11 and what they represent:

QSEP – The amount of heat used to decompose the fuel into its elemental form. This heat is taken away from combustion in the yield reactor, which simulates the combustion reactions.
QRAD – The radiant heat from the boiler used to boil water and superheat steam. (Set to equal QRAD2 via a design specification).
QECON – Convective heat sent to bring boiler feed water separated away from radiant heater to its boiling point. (Set to equal QECON2 via a design specification).
QEVAP – Convective heat used to evaporate water. (Set to equal QEVAP2 via a design specification).
QSH – Convective heat used to superheat the steam. (Set to equal QSH2 via a design specification).

A4. Pressure Swing Adsorption 15 MW Biomass Plant Model

The concept of a PSA with an outlet stream of 40% oxygen entering the furnace was modeled using Aspen Plus. Pressure Swing Adsorption is a non-cryogenic way of purifying gas. Special adsorptive materials (e.g. zeolites) are used as a molecular sieve, preferentially adsorbing the undesired gases at high pressure. Although it operates at near ambient pressure, it is unable to reach near the oxygen purity of cryogenic air separation.

The PSA used only 0.5 MW of auxiliary power. However, this savings was greatly overcome by the 4.5 MW needed for compression to bring the outlet stream from 35 psia to 800 psia. This was due to the high volume of gas flow through the multi-stage compressor. Other disadvantages of PSA included the product recovery train when carbon capture was necessary. Since there was more nitrogen in the stream than oxyfuel, the volumetric flow rate through the pipes in the furnace outlet were significantly higher. The extra nitrogen in the stream would defeat the purpose of capturing carbon dioxide in a simplified manner.

Figure A1 Combustion Cycle in 15 MW Conventional Biomass Model

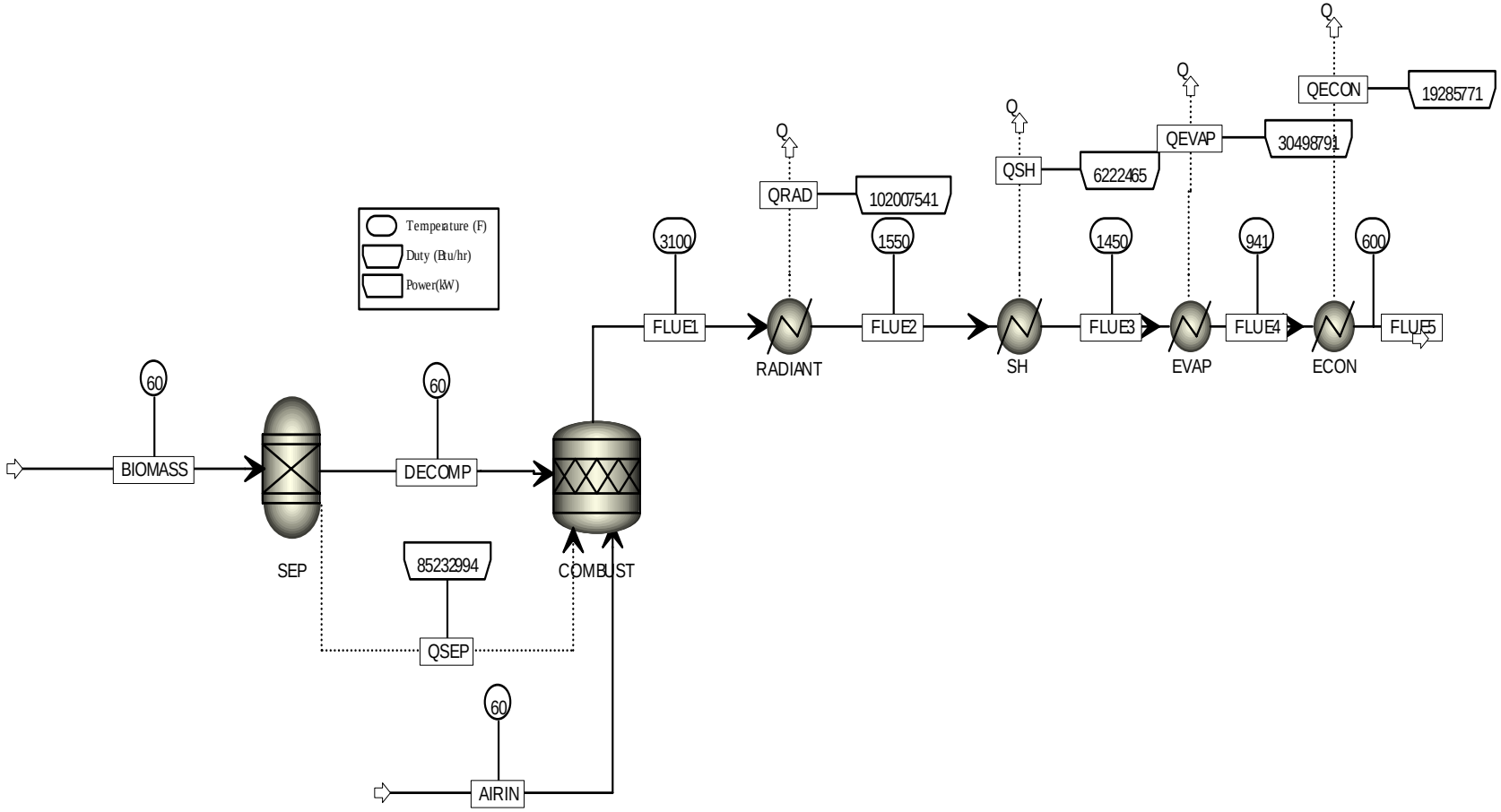
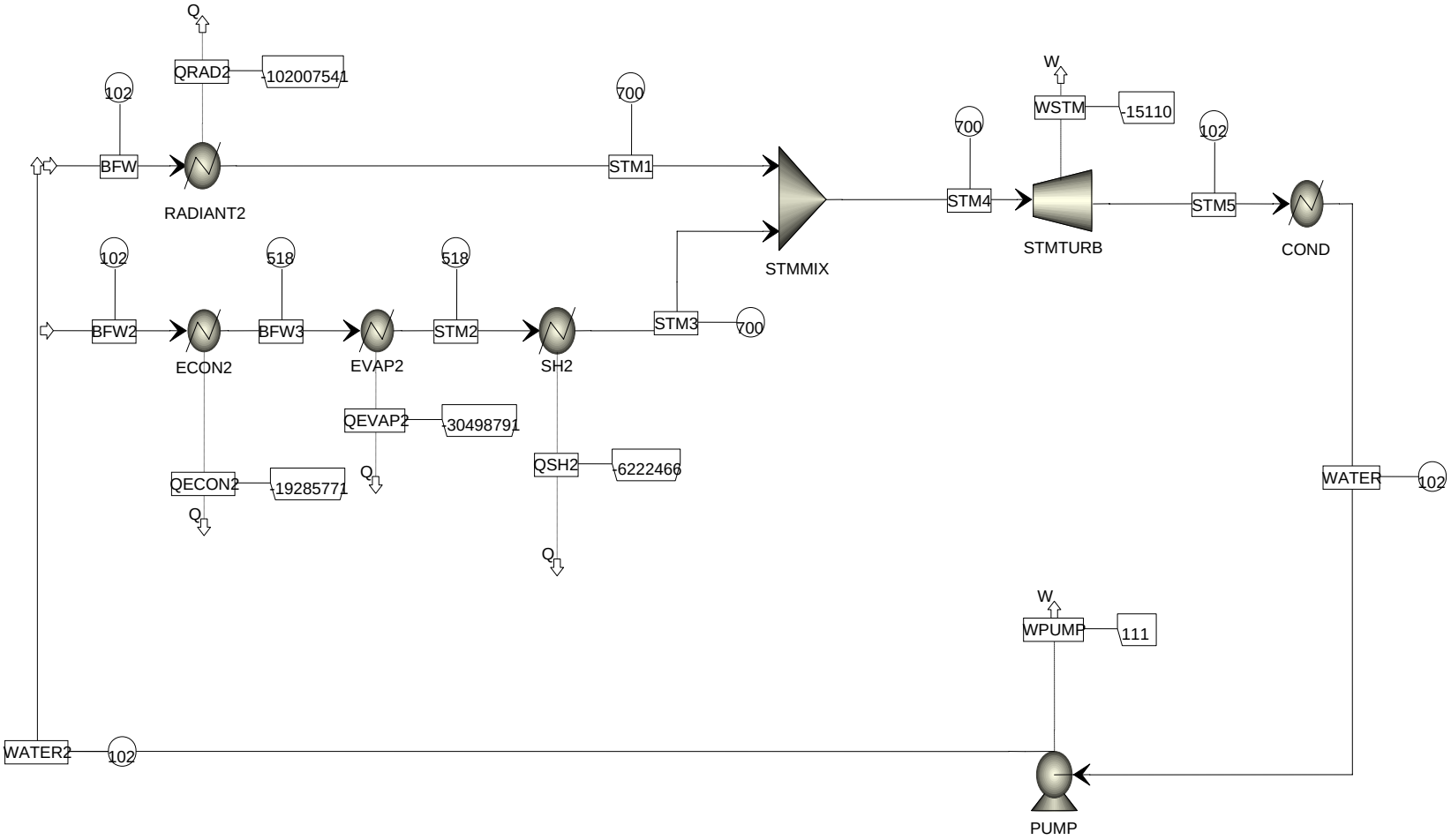


Figure A2 Steam Cycle of 15 MW Conventional Biomass Plant



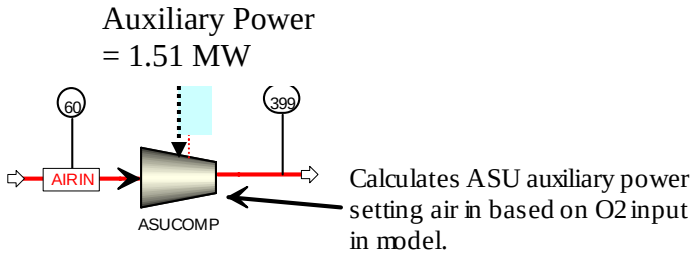
A5. Pressurized Oxyfuel 15 MW Biomass Model

The pressurized oxyfuel (TIPS) plant was the main focus of this study. The process modeling performed using Aspen Plus solidified the theory regarding the ability of a pressurized oxyfuel plant to recover energy from biomass. Using the same Rankine Cycle as the conventional model for the heat balance, TIPS used less fuel (262 tons/day of wood waste compared to 290 tons/day) to produce the same net power (15.0 MW) and was able to capture 220 tons day of CO_2. In addition to that, the TIPS plant produced 26 tons/day of 8-pound steam exchanging 700 kW of external heat. This gave TIPS a net efficacy of 28.6% compared to 24.7% for the conventional case and 220 tons/day of liquid CO_2 product. The conventional plant was not able to capture CO_2. The steps of the process are prepared individually to build the overall model in Aspen. This presents the opportunity to discuss each step individually.

A5.1 ASU

For this study, the ASU Auxiliary Power was estimated by using the compression energy to bring enough air to 5 bar to supply the 95% oxygen stream needed for combustion. There is more detail that goes into an ASU auxiliary power calculation, but the compression energy provides a fair estimate. This method was used by NETL in their 550 MW atmospheric oxyfuel model. Figure A3 shows the Aspen model of the ASU compression. It was necessary to compress 749 tons/day of air to provide the 174 tons/day of oxygen needed for combustion. The auxiliary power usage was 1.51 MW.

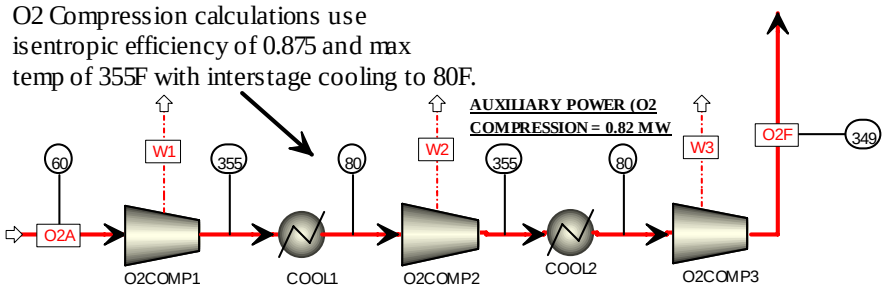
Figure A3 ASU Compression Simulation in Aspen Plus



A5.2 Oxygen Compression

A 3-stage compressor with interstage cooling was modeled for compression of the 95% oxygen stream from 14.7 psia to the operating pressure of 800 psia. The maximum temperature within the compressors was set at 355°F and interstage cooling was set to 80°F. The isentropic efficiency of the compressors was assumed to be 0.875. The auxiliary power usage was 0.82 MW. Figure A4 shows the schematic used in the Aspen Plus model.

Figure A4 Oxygen Compression Simulation in Aspen Plus



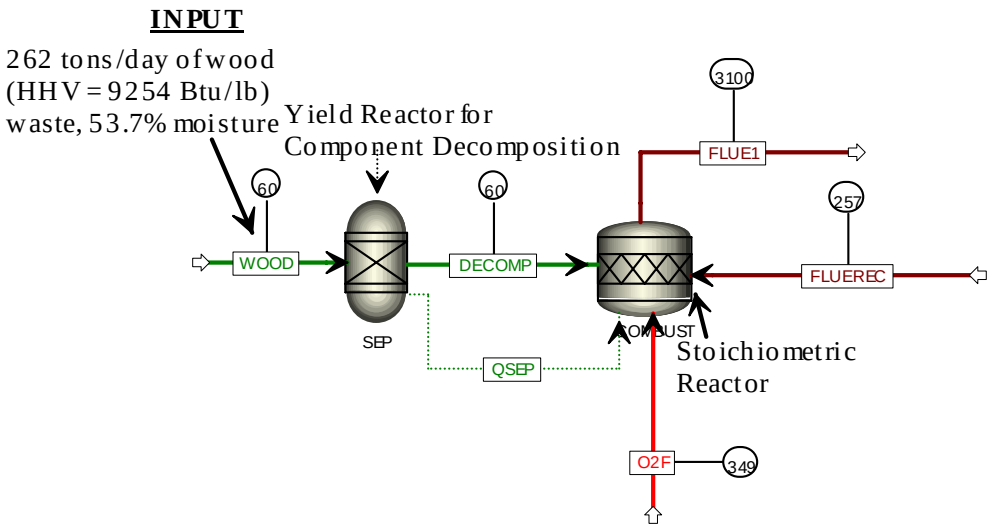
A5.3 Wood Combustion

A yield reactor, which allows a user to specify temperature, pressure, and component yields from fossil fuels, was used to simulate component decomposition from the wood waste and a stoichiometric reactor, which generated combustion products by reacting carbon, hydrogen and sulfur with oxygen, was used to simulate combustion with the 95% oxygen stream. The excess oxygen was input through a design spec to keep it at 0.042%. The pressurized system requires less oxygen to keep the same oxygen partial pressure in the outlet stream. A recycle stream was input to simulate the CO_2 rich stream after the condensing heat exchanger cooling down the furnace outlet gas. Enough recycle was input to maintain a furnace outlet temperature of 3100°F. The reactions used for combustion were:

- $C + O_2 \rightarrow CO_2$
- $H_2 + 1/2\ O_2 \rightarrow H_2O$
- $S + O_2 \rightarrow SO_2$

Figure A5 shows the schematic of the wood combustion unit operations used in Aspen Plus. 262 tons/day of wood were combusted with 174 tons/day of the 95% oxygen stream and 1720 tons/day of the CO_2 rich recycle stream (further explanation shown in Figure A9 and Figure A13).

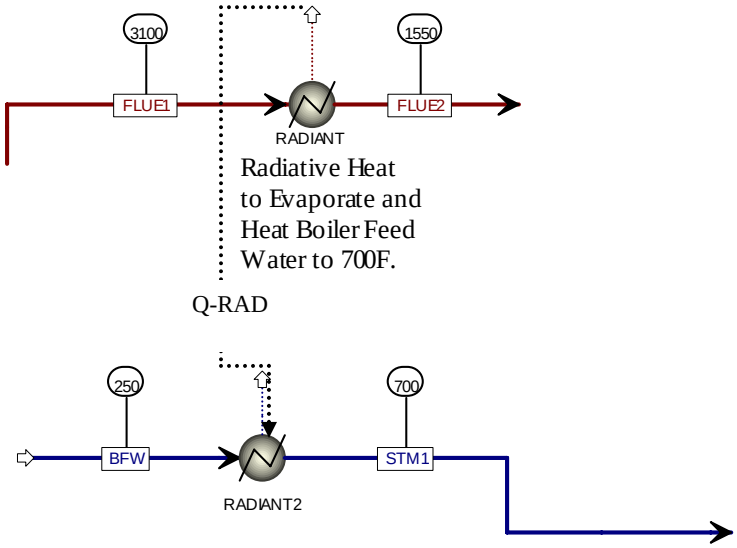
Figure A5 Wood Combustion Simulated in Aspen Plus



A5.4 Radiative Heat Exchanger

Radiative heat from the flue gas was used to boil and heat up 1,043 tons/day of feed water from 250°F to 700°F. The model calculate that 9.74 * 10^7 Btu/hr of heat was supplied by cooling 2,164 tons/day of the flue gas from 3100°F to 1550°F. The heats were balanced by using a design spec in Aspen Plus. Figure A6 shows the schematic used in Aspen Plus to simulate the radiative heat exchange.

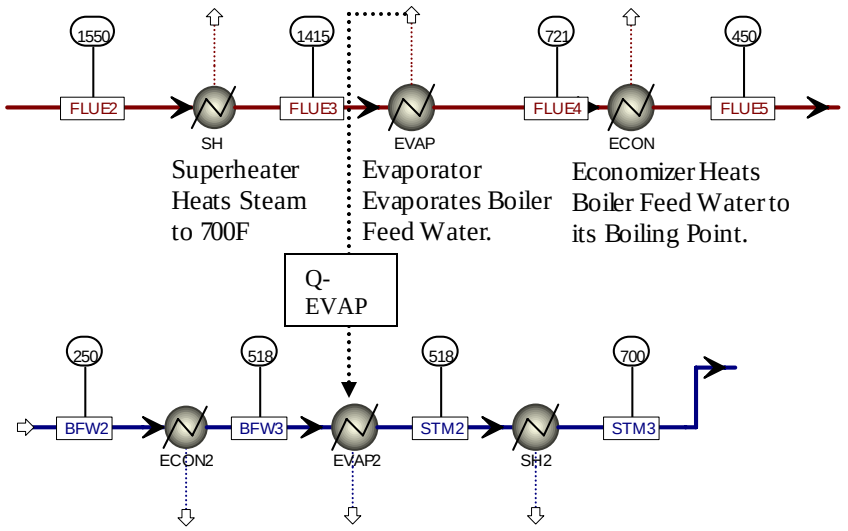
Figure A6 Radiative Heat Exchanger Used in Aspen Plus



A5.5 Convective Heat

The convective heat was simulated in a similar way to the radiative heat. It was split into an economizer to bring the boiler feed water to its boiling point, an evaporator and a superheater to bring steam to 700°F. 681 tons/day of feed water was boiled and heated to 700°F by cooling 2,164 tons/day of flue gas from 1550°F to 450°F. Figure A7 shows the schematic for convective heat exchange used in Aspen Plus.

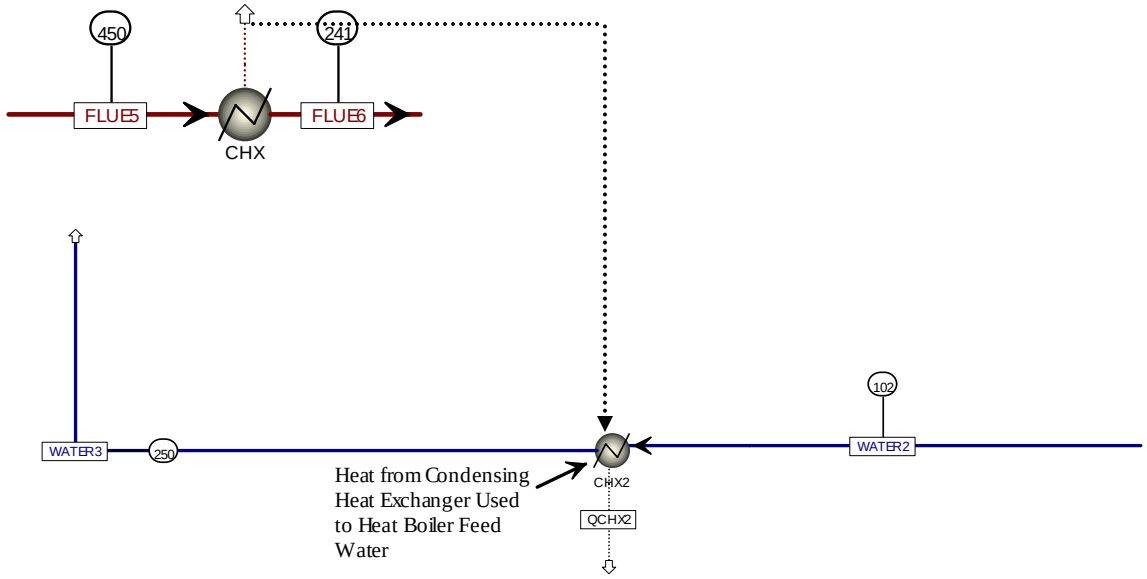
Figure A7 Convective Heat Exchange Simulated Using Aspen Plus



A5.6 Condensing Heat Exchanger

The condensing heat exchanger is one of the key unit operations in the pressurized oxyfuel system. It is unavailable in conventional ambient power plants. However, since TIPS is able to fully utilize the latent heat of vaporization of water, it can heat the boiler feed water using heat of condensation. This was simulated in Aspen Plus by cooling the flue gas down to about 241°F. 2,164 tons/day of flue gas was cooled from 450°F to 241°F and 82.2% of the water was condensed while heating the boiler feed water from 102°F to 250°F. Figure A8 shows the schematic used in Aspen Plus for the condensing heat exchanger.

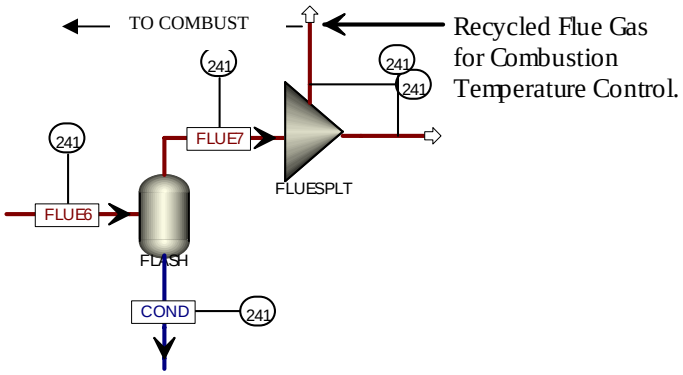
Figure A8 Condensing Heat Exchanger Simulated Using Aspen Plus



A5.7 Flue Gas Recycle

The amount of flue gas available for recycle was calculated by separating the gaseous stream from the liquid stream using a FLASH separator and the Peng-Robinson Equation of State in Aspen Plus. A splitter was input into the model to allow for calculation of the fraction split to maintain the combustion temperature of 3100°F. The result was about 55% of the flue gas being split to go back to the furnace. Figure A9 shows the schematic used in Aspen Plus for the flue gas recycle calculation (output is shown in Figure A5 as FLUEREC).

Figure A9 Flue Gas Recycle Simulation in Aspen Plus

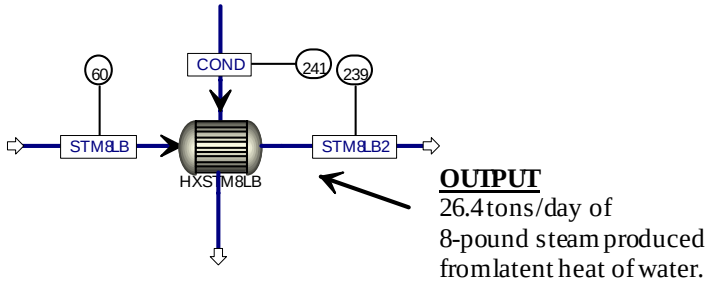


A5.8 Additional Steam Production

Another key to the pressurized oxyfuel process is the ability to use the remaining heat of the condensate to produce an additional amount of 8-pound steam at 239°F. It could use this externally exchanged heat for other applications, but since 8-pound steam is a commonly used

product, this was used as a practical application. 26.4 tons/day of 8-pound steam was produced by cooling the condensate from 241°F to 61°F. Figure A10 shows a schematic of this calculation used in Aspen Plus.

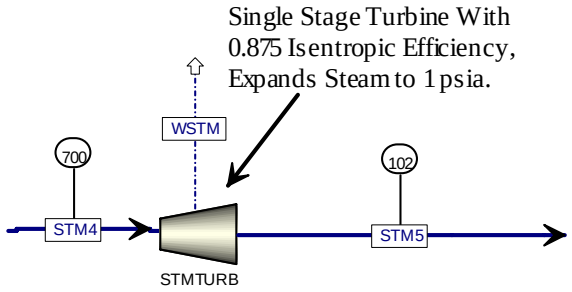
Figure A10 8-pound Steam Production Simulated Using Aspen Plus



A5.9 Steam Turbine

For this study, a single stage turbine was used with 0.875 isentropic efficiency. By expanding the 765 psia, 700°F steam to 1 psia, the turbine generated 17.4 MWe while cooling the steam to 102°F, which is realistic as most areas have cooling water at or below 85°F. Figure A11 shows the schematic used for the steam turbine in Aspen Plus.

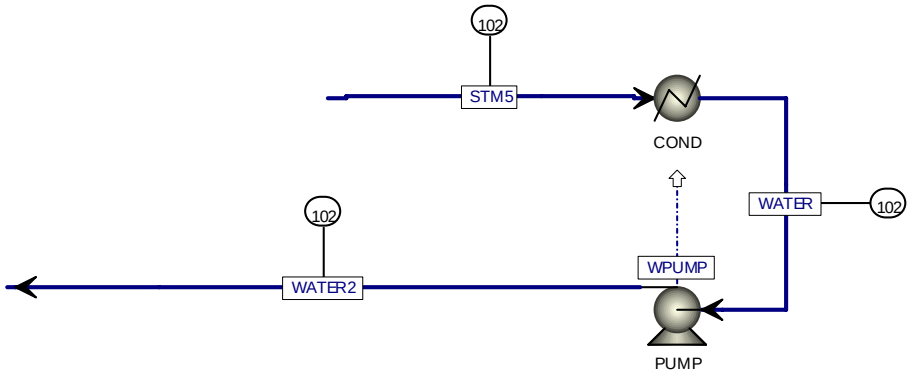
Figure A11 Steam Turbine Simulation in Aspen Plus



A5.10 Condenser and BFW Pump

Following the Steam Turbine, it was necessary to install a condenser prior to the BFW Pump. The condenser was assumed to have no pressure drop. The pump raised the pressure of the feed water from 1 psia to 895 psia with a pump efficiency of 0.875. This used 110 kW of auxiliary power. Figure A12 shows the schematic used for the condenser and BFW Pump in Aspen Plus.

Figure A12 Condenser and BFW Pump Simulated in Aspen Plus



A6. Aspen Plus Model of TIPS

The process modeled in this case is a 15 MW net electrical wood waste Pressurized Oxy-Fuel plant which is based on an average proximate analysis, ultimate analysis, and sulfur analysis of wood waste in the Pacific Northwest. Aspen Plus 2004 was the executive interface used to model this pressurized oxy-fuel system.

Aspen Plus 2004 went through several iterations using the secant method and solved simultaneously for 10 different design specifications. The following are the 10 different design specifications and how they were solved in order.

1. AIRIN – The amount of air needed was solved by setting the oxygen in the air separation phase equal to the oxygen entering the combustor. This took 47 iterations and solved with an error of 0.
2. BFW2 – The boiler feed water entering the ECON heat exchanger was solved by specifying a temperature of 450°F for FLUE5T and varying the boiler feed water until this specification was met. This took 310 iterations and solved with an error of 1.31e-7.
3. QCHX - The heat duty of the condensing heat exchanger was set by varying the heat duty to the flue gas from the condensing heat exchanger until it equaled the amount of heat it took to heat the boiler feed water to 250°F. This took 65 iterations and had 0.0092 error.
4. QECON – The heat duty of the Economizer was set on the flue gas side by setting it equal to the amount of heat necessary to bring the water entering the Economizer to its dew point. This took 1467 iterations and had 0 error.
5. QEVAP – The heat duty of the Evaporator was set on the flue gas side by setting it equal to the amount of heat necessary to vaporize the water entering the evaporator. This took 1465 iterations and had an error of 0.
6. QSH – The heat duty of the Superheater was set on the flue gas side by setting it equal to the amount of heat necessary to heat the steam entering the superheater to 700°F which is the specification for a steam turbine in a 15 MW plant. This took 1 iteration and had an error of 0.041.

7. QRAD – The heat duty of the Radiant heater was set on the steam side by setting it equal to the amount of heat from cooling the combustion exit gas from 3100°F to 1550°F. This took 43 iterations and had 0 error.
8. RECYCLE – The amount of recycle mass flow was set by setting the combustion outlet temperature to 3100°F. This took 193 iterations and had an error of 0.0025.
9. BFW – The amount of boiler feed water entering the radiant boiler was set on the steam side so that the steam exiting the radiant boiler was 700°F while keeping the heat balanced. This took 79 iterations and had an error of $9.09*10^{-9}$.
10. O2IN – The amount of oxygen entering the combustor was set by having 4.2 ppm O2 in the flue gas stream. This took 50 iterations and had an error of $1.72 * 10^{-6}$.

The feedstock was based on an average composition of wood waste in the Pacific Northwest. Table A2 lists the proximate, ultimate, and sulfur analysis used in the model.

- A list of technical assumptions used in the model:
    - Ambient Conditions: 60°F, 14.7 psia
    - Pressure Drop on Flue Gas Side = 0 psi
    - Pressure Drop on Steam Side across Radiant Boiler = 80 psi
    - Pressure Drop on Steam Side across Superheater = 30 psi
    - Pressure Drop on Steam Side across Evaporator = 0 psi
    - Pressure Drop on Steam Side across Economizer = 50 psi
    - Pressure Drop on Steam Side across Condensing HX = 50 psi
    - All reactions and heat exchange occur at steady state.

Component Level Models and Sub-Level Models

a. Air Separation

An isentropic compressor (isentropic efficiency = 0.875) was used to compress enough air so there was the correct amount of oxygen entering the combustor at 72.5 psi. The work was calculated for this requirement and was used in the auxiliary power calculation which was used in the net electricity calculation. The ASU auxiliary power calculated in this case was 1.51 MW.

b. Oxygen Compressor

A 3 stage compressor to compress 15,495 lbs/hr of a 95:5 Oxygen:Argon mixture (the nitrogen was assumed to be separated in the ASU) from 14.7 psi to 800 psi was simulated using a multi-stage compressor in Aspen Plus. The maximum temperature in the air compressors was 355°F. Stage 1 used 290 kW to compress the mixture to 61 psi, stage 2 used 270 kW to compress it to 224 psi, and stage 3 used 264 kW to compress it to 800 psi.

c. Pressurized Fluidized Bed Combustor (PFBC)

Two reactors in series were used to simulate the PFBC. They were RYIELD and RSTOIC which were both available in Aspen Plus. The RYIELD is a mass yield reactor which allows for pressure, temperature, and component yield specifications. This was used to calculate the amount of heat required to decompose the biomass into its elemental form. RSTOIC is a stoichiometric reactor which generates combustion products adiabatically and the temperature is controlled by recycled flue gas. The fuel was fed and the composition was determined according to the data in Table 1. It was determined that it took 21,800 lbs/hr of wood to produce a net of 15 MWe. RYIELD was used to model the decomposition of biomass at the bottom of the PFBC. The component yields were assumed to be 0.537 H_2O, 0.009 Ash, 0.236 Solid Carbon, 0.0279 H_2, 0.003 N_2, 0.0018 S, and 0.1853 O_2 (total 1.00) based on the composition of wood waste. RYIELD was specified at 800 psi and 60°F. The decomposition heat calculated from RYIELD was combined with the heat of combustion calculated by RSTOIC to simulate adiabatic combustion with recycled flue gas controlling the temperature to 3100^{o}F. The operating temperature of RSTOIC was assumed to be 3100F, and the pressure was 800 psi. The reactions (C(Csolid) + O_2 → CO_2, H_2 + 1/2 O_2 → H_2O, and S + O_2 → SO_2) were all assumed to reach completion with no byproducts.

d. Radiative and Convective HX

Two Heaters were used to simulate the countercurrent heat exchanger which used the radiative heat from combustion to boil and superheat water in the Rankine Cycle. The design spec QRAD described in section 2 was used to balance the heat. The flue gas inlet temperature was 3100°F and its exit temperature was specified to 1550°F, and the boiler feed water entered at 250°F and 845 psi and exited at 700°F and 765 psi. The convective heat exchanger completed the vaporization and superheated the steam before it entered the turbine. It boiled and superheated 86,944 lb/hr of water to 700°F. The heat duty used in QRAD was $9.74 * 10^7$ Btu/hr.

e. Superheater

Two Heaters were used to simulate the countercurrent heat exchanger used to superheat steam in the Rankine Cycle from 518°F to 700°F. This used $7.99 * 10^6$ Btu/hr of heat and cooled the flue gas from 1550°F to 1415°F. The pressure dropped from 795 to 765 psi on the steam side. This was an assumption based on CANMET's simulation of a 15 MW biomass plant.

f. Evaporator

Two Heaters were used to simulate the countercurrent heat exchanger used to evaporate the boiler feed water in the Rankine Cycle. This used $3.92 * 10^7$ Btu/hr of heat and cooled the flue gas from 1415°F to 721°F. There was no pressure drop in the evaporation of water.

g. *Economizer*

Two Heaters were used to simulate the countercurrent heat exchanger used to heat the boiler feed water from 250°F to its dew point of 518°F. This used $1.64 * 10^7$ Btu/hr of heat and cooled the flue gas from 721°F to 450°F.

h. *Condensing Heat Exchanger*
Two Heaters were used to simulate the countercurrent heat exchanger used to cool the flue gas to under its dew point so that most (82.2% in this case) of the water is recovered as a liquid. The boiler feed water is heated to 250°F and this used $2.12 * 10^7$ Btu/hr of heat. This cooled the flue gas down to 241°F and a vapor fraction of 0.831. A FLASH unit was used following the HEATER to separate the gas from the liquid on the flue gas side.

i. *Steam Turbine*
An isentropic Turbine was used to simulate the steam turbine which expanded 177,997 lb/hr of steam at 700°F and 765 psia to 1 psia and cooled it down to 102°F. This produced 17.4 MW of gross power.

j. *Condenser*
A HEATER was used to simulate the steam condensation in the Rankine Cycle at 102°F. and 1 psia. The cooling duty was $1.23 * 10^8$ Btu/hr.

k. *BFW Pump*
A PUMP was used to simulate 143,673 lb/hr of boiler feed water being pumped from 1 psia to 895 psia. This consumed 128 kW of auxiliary power.

l. *Heat Exchange for 8 pound steam production*
A HEATX was used to simulate 2,200 lb/hr of 8 pound (22.7 psia) steam using the hot condensate from the condensing heat exchanger. $2.49*10^6$ Btu/hr of heat was exchanged from the condensate to the 8 pound steam.

m. *Flue Split*
A SPLIT unit was used to simulate splitting enough flue gas off of the back end to keep the combustion temperature at 3100°F. 143,249 lb/hr of a CO_2 rich (97.5% by weight) stream was recycled to the combustor.

The Peng-Robinson EOS, as referenced in footnote 1, was used on the flue gas side. This was used to calculate temperatures, enthalpy, vapor fraction, phases of individual components, volume, and density.

The NBS/NRC Steam Tables were used for the entire Rankine Cycle to calculate steam temperatures, enthalpies, vapor fraction, volume, and density.

A7. Conclusions and Recommendations

Figure 1 is the process flow diagram of the flue gas combustion side of the model. Appendix I at the end of this report shows a complete stream analysis for the model. Underneath the oxygen compression is air being compressed to 72.5 psi for air separation. This is for the purpose of calculating auxiliary power due to compression work for the ASU plant. The oxygen is sent

through 3 stages of compression (800 psi) before reaching the RSTOIC which simulates the combustion reactions. Prior to the fuel entering RSTOIC, it enters RYIELD which simulates the decomposition into its elements and the energy it takes for decomposition is subtracted from the combustion energy. The flue gas is then sent through a series of heat exchangers (Radiant, Superheater, Evaporator, Economizer, and Condensing Heat Exchanger) and balances its heat with the steam in the Rankine Cycle. The flue gas coming out of the Condensing Heat Exchanger is mostly liquid and is sent into a FLASH to separate out the liquid (82.2% of H_2O entering condensing heat exchanger comes out as liquid). The hot condensate is then sent to a HEATX model to simulate the external exchange of heat to 8 pound steam. 79.4% (Mass Basis) of the flue gas is recycled back to the combustor to keep the combustion outlet temperature at 3100°F.

Figure A2 is the process flow diagram of the Rankine Cycle side of the model. Water from the condenser at 102°F and 1 psia enters a pump which pumps the water to 895 psia. The water then enters the condensing heat exchanger which heats it to 250°F while cooling and condensing the flue gas. The boiler feed water is then split so that part of it enters the radiant boiler so that it exits as 700°F steam at 765 psia and the other part goes through the Economizer, Evaporator, and Superheater and is also heated to 700°F and 765 psia (The mass flow is based on the setting for the flue gas temperature entering the condensing heat exchanger). The two 700°F, 765 psia steam streams are then mixed and sent through a turbine where the steam is expanded to 1 psia. It is then sent through the condenser and the cycle continues.

Furthermore, the Multi-Product System Efficacy was calculated as follows:

- 5.2 CHP (Combined Heat and Power)
- Fuel In = 21,800 lb/hr, HHV = 8,603 Btu/lb
- Energy In = $1.88 * 10^8$ Btu/hr or 151 MW
- Gross Power (Steam Turbine) = 17.5 MW
- Auxiliary Power = 2.5 MW
- Net Power = 15.0 MW
- Externally Exchanged Heat (8 pound steam) = 0.73 MW
- Emissions: $SO_2 = 6.81 * 10^{-7}$ kg/kJ

Net CHP (Combined Heat and Power) *Efficacy*[2] = $\frac{(15.0 + 0.73)\text{MW out}}{55.0\text{ MW in}}$ = 28.6%

The results of this study clearly show the advantages of using TIPS with 53.7% moisture wood waste as the fuel. TIPS not only has a higher efficiency than a conventional biomass power plant, but it also can be operated in a combined heat and power mode where it can produce 8-pound steam with the latent heat recovered from the flue gas. It also has a carbon capture option while maintaining a very favorable efficiency advantage (28.6% to 24.7%) over the conventional plant. Since the flue gas is already at 800 psi, it would simply need to be cooled to 80°F to produce a liquid stream and pumped to the CO_2 product pressure of 2200 psi. This would only use about 0.5% of the net power in energy consumption.

[2] Net CHP Efficacy = (net electrical energy + externally exchanged heat)/(Total heating value energy of all direct and indirect input fuels)

Most of the unit operations in this system are known or proven and do not provide obstacles to the design of a TIPS plant. Pressurized Fluidized Bed Combustors (PFBCs) have been used for pressurized combustion in the past, and several are in operation internationally today. Since the biomass in this case is 53.7% moisture, a slurry pump could be used to input biomass at 800 psi. 50% solids slurry pumps are common and do not pose a major technological challenge. The condensing heat exchanger materials have been tested at the University of Nevada-Reno (UNR) and are capable of withstanding the conditions that the TIPS process would provide. Future work must include emissions studies although it presents less of an issue using wood waste as the fuel due to its low sulfur content (0.903). Wood ash condensation is a phenomenon that must be experimentally evaluated.

A8. References

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[4] McGurl, G., James, R., Parsons, E., Ruether, J., Wimer, J. "Quality Guidelines for Energy System Studies," Original Document – February 24, 2004, Revision Date – January 30, 2005.

[5] Zheng, L., Pomalis, R., Clements, B. "Feasibility Study of ThermoEnergy Integrated Power System (TIPS) Process," November 23, 2006.

Figure A13 Combustion side of 15 MWe Wood Waste Fueled Pressurized Oxy-Fuel Aspen Model

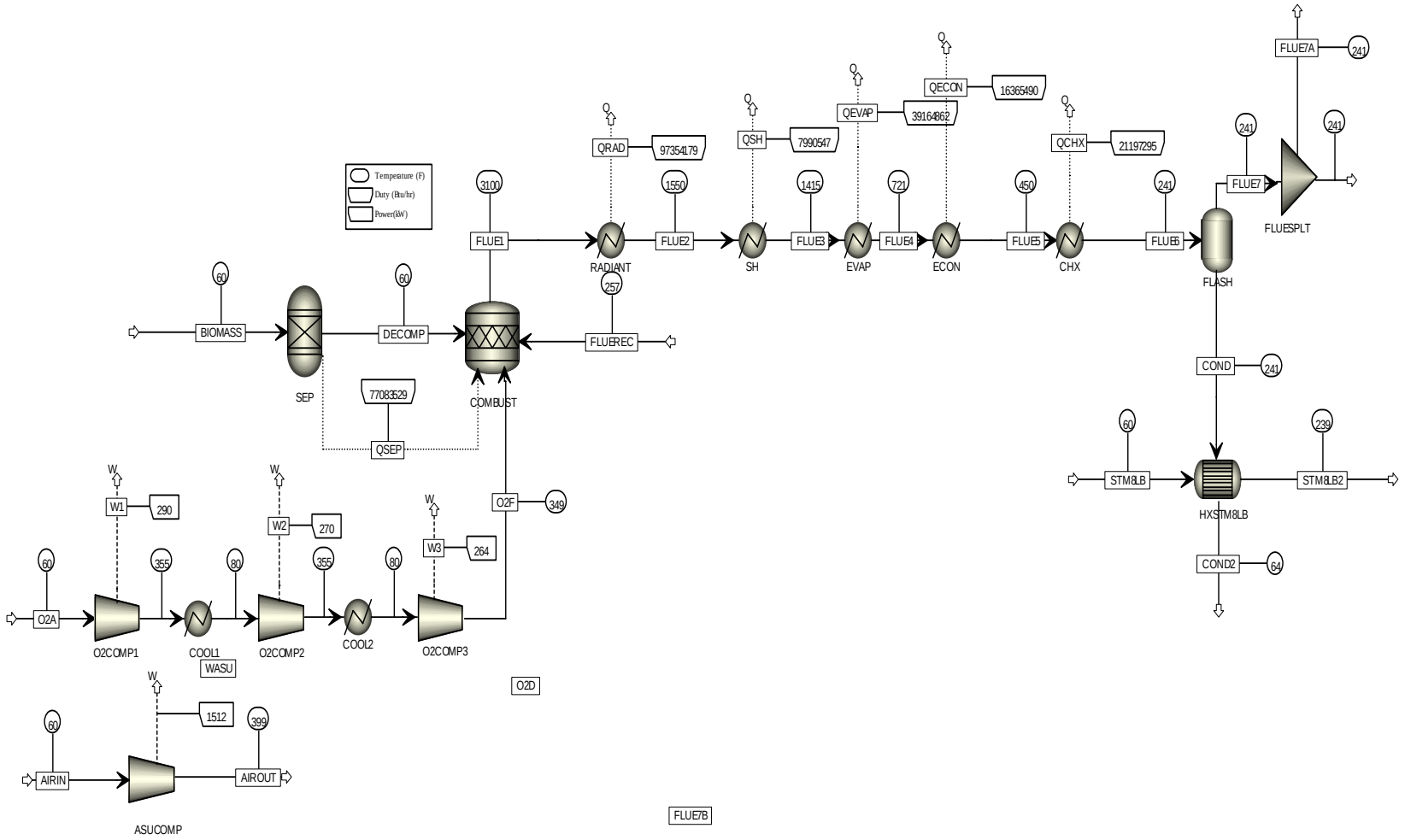
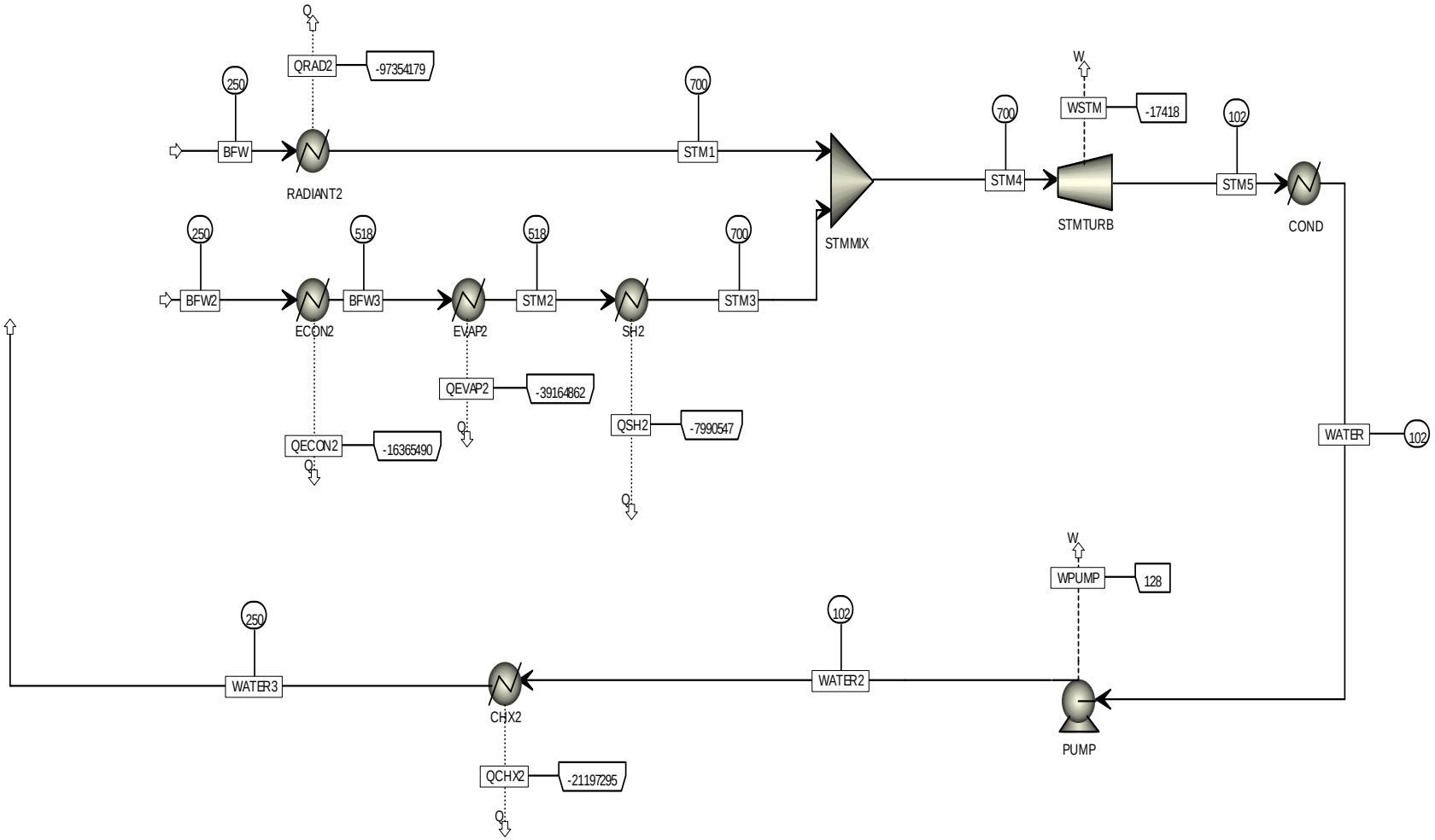


Figure A14 Rankine Cycle side of the 15 MWe Wood Waste Fueled Pressurized Oxy-Fuel Aspen Model



Part B: Heat Exchanger Materials

B1. Executive Summary

A prospective new generation power plant design called the TIPS process is being investigated for combusting waste biomass. A key unit operation of TIPS is the condensing heat exchanger. This unit operation has been predicted to reduce the combustor offgas temperature from as high as 1200°F to 572°F or lower to condense much of the water vapor. This hot, predominantly steam and CO_2 gas may contain small concentrations of H_2SO_4 and HCl due to the combustion of the sulfur and chlorine containing compounds in the feed biomass. The heat exchanger condenses water from the steam which will contain the acids listed above. Such hot acidic water presents serious corrosion issues for the surfaces of the condensing heat exchanger.

Experiments were conducted under a range of conditions expected during operation of the condensing heat exchanger. These conditions were determined by simple calculations making gross assumptions prior to modeling the process sequence with the Aspen program. The result was that the temperatures predicted for the condensing heat exchanger were higher (483-572°F) than the Aspen predicted range of 241-450°F. Because the temperatures tested were above the Aspen values, the results would be applicable to the TIPS plant although other materials might also be considered.

Titanium nitride (TiN) coated copper and 303 stainless steel, commercially pure titanium, and grade 7 Titanium (Ti-0.2% palladium) coupons were heated for three days each at several gas compositions over the temperature range of 482-572°F. These samples were then observed in a scanning electron microscope for visual and chemical evidence of corrosion. The two titanium samples appeared to withstand the treatments whereas the TiN coated copper and stainless steel samples were severely corroded.

B2. Introduction: Condensing Heat Exchanger

Most of the TIPS unit operations are proven in existing industrial applications or under active development. Central to the success of TIPS is the condensing heat exchanger. It collects particulates, acid gases and mercury into a condensed phase that is roughly 2,500 to 3,500 times smaller than the volume of gas treated by conventional atmospheric pressure flue gas clean-up systems. Operating conditions experienced by the condensing heat exchanger are so severe that conventional heat exchanger materials most likely will fail shortly after being placed in service. Potential materials substitutions are available that, if successful, would assure that the TIPS condensing heat exchanger would not fail.

Corrosion is best characterized as a chemical reaction in which electron transfer occurs between the oxidizing species and the reducing species. The critical parameters that make corrosion rates faster are 1) acidity, 2) temperature, and 3) oxidation potential. This means the harsh conditions in the condensing heat exchanger are perfect for corrosion of metals—making the selection of the most resistant material a must. From an engineering approach, there are several methods that could be employed to protect the metal of the heat exchanger, such as galvanic coupling,

sacrificial anodes, surface coatings, but many of the standard practices are not feasible in this environment, or application. Instead, we must choose a more corrosion resistant metal to withstand the high temperature, low pH conditions. Materials that have an inherent passivating layer or artificial protective layer are most likely to be the best. Metals are excellent conductors, but metal oxides are electrically insulating. Even a thin layer of metal oxide (passivated metal) will protect the bulk metal by stopping the transfer of electrons. There are many examples in use today. Stainless steels have a natural oxide formed by the alloying agent Cr; aluminum forms an oxide layer instantly when exposed to air. Titanium, tantalum, and niobium are examples of metals that are protected in harsh atmospheres by the formation of the passive layer. The goal of this project is to not only identify candidate materials, but find the best which are still economical and practical to use.

Conventional heat exchangers are commonly constructed of a metal or an alloy. Austenitic stainless steel (304, 316, etc) is often used when mildly corrosive liquids are encountered. The condensing heat exchanger material must be resistant to acidic corrosion, transfer heat well and resist scale formation from the entrained solids contained in the gas feed. Conventional 316 stainless steel is not expected to be sufficiently stable for the service expected of the condensing heat exchanger. Most other refractory metal heat exchanger materials are unlikely candidates for the condensing heat exchanger for the same reason. The most promising metal would be titanium or alloys of titanium.

The following is a discussion of potential condensing heat exchanger materials for the TIPS system. Stainless steel is typical of metallic heat exchange material except that it offers very good corrosion resistance compared to other metals. The thermal conductivity of stainless steel is about 20 W/m*K which is mediocre for a metal. For example the thermal conductivity of iron is about 40, aluminum is about 240 and copper about 400 W/m*K, respectively. The resistance to scale formation for stainless steel is about average for a nonreactive metal. Its yield strength remains above 50% of the room temperature value at up to 1112°F. It is not brittle and is easily welded.

Grade 7 Titanium (Ti-0.2pct Pd) is probably the most corrosion resistant of the titanium alloys. It has heat exchange characteristics similar to stainless. It is considerably more expensive than stainless steel however (historically, stainless steel can be purchased for $10/sq. ft., while Ti sheet is typically more than $30/sq.ft.).

Coated heat exchangers offer potentially better performance than conventional metal alloys. This is because the substrate material can be designed for optimal heat exchange and mechanical characteristics and the coating designed for optimal corrosion resistance.

Teflon coated stainless steel heat exchangers would appear to be a good possibility for TIPS. This technology has been perfected through the pilot stage and appears to provide the protection necessary against the action of the dilute mixed acid solution at 572°F. Teflon coated heat exchangers are available commercially. Teflon is a chemically inert plastic that has a maximum continuous operating temperature of 500°F (1). Its thermal conductivity is 0.20 W/m*K. The maximum working temperature is about 54°F, too low for use in the TIPS system. Its poor

thermal conductivity is also a detriment. Teflon's very low friction and chemical inertness indicate that it would not form much of a scale layer.

Physical vapor deposition (PVD) coatings appear to be promising for the condensing heat exchanger. The coating process is low cost and some coatings may offer the required surface protection. Candidates for PVD coating materials include TiN and diamond-like coatings. Both coating materials are hard and are reported to be inert to acids (2,3). Diamond-like coatings offer the additional advantages of being nearly frictionless and have the highest heat transfer coefficient of any material, approximately four times higher than copper. Because these coatings are thin, they must have a substrate metal backing them to provide structural support. A high heat transfer material such as copper would be a likely candidate for the substrate material. Such a heat exchanger would be highly efficient and stable.

TiN is applied by arc plasma vaporization of titanium under vacuum (4,5). Nitrogen gas is admitted to the reactor under controlled flow such that TiN forms and adheres chemically to the surface of the part being coated. The coated part is under a negative electrical potential to attract the ions. The TiN coating is chemically inert and can be applied at relatively low temperatures with a minimum of porosity. This makes it an excellent candidate coating material for the condensing heat exchanger.

Current technology for diamond-like coatings (6,7,8) is that they can be applied stress free on small areas of substrate metals by several techniques. An interesting deposition method is called hollow cathode plasma immersion ion processing (HCPIIP) (6). This approach uses hollow cathode technology with rapidly pulsed fields to form uniform diamond-like films from hydrocarbon plasmas on complex shaped substrate materials near room temperature. The inert, low porosity diamond-like films have excellent adhesion, extremely high heat transfer rates and low friction. Such films appear to be ideal for coating the condensing heat exchanger surfaces of the TIPS process. However, the design for the condensing heat exchanger will require that the process gases pass over the outside of cooling tubes rather than through them. HCPIIP technology is only applicable to coating the insides of tubes and is not available for the TIPS application. Conventional diamond coating of large complex assemblies is not perfected at this time so diamond coating was not investigated further.

Plasma coating of inert substances on heat exchanger surfaces was also considered. The current technology is not advanced sufficiently to assure that complex shaped assemblies such as the condensing heat exchanger can be coated uniformly. Furthermore, porosity is still a problem for plasma coating. The current technology employs an organic material to fill the pores. There are no known pore-filling organics that will withstand the conditions seen by the TIPS condensing heat exchanger. Consequently, plasma coating was not included in this study.

Review of the above discussion on heat exchanger materials for use in the TIPS system leads to the conclusion that titanium or titanium alloys and TiN coated materials are worthy of laboratory testing to ascertain their resistance to corrosion in the TIPS system. The coated materials offer better heat transfer and are probably less expensive, but are somewhat unproven with regard to chemical resistance or to delamination of the coating. Titanium looks promising from corrosion and fabrication aspects, but has poorer heat transfer characteristics and is more costly.

B3. Materials and Procedures

A 2-liter Parr Instruments Company, Model 4521 autoclave was used as the pressure vessel in these experiments. The bomb and all internal parts were machined from Grade 4 titanium. The autoclave was equipped with a thermowell that extended halfway to the bottom of the reactor for temperature measurement. It also had a valved gas port for filling the reactor with gas and for releasing gas when an experiment was completed. A gold-faced Inconel burst disc, rated at 2000 psi, was fitted. A blast diversion shroud was attached to vent steam if the burst disc failed. The head was water cooled.

All sample coupons were of commercial purity and obtained from commercial vendors. They measured 1 ½ by 2 ½ inches and were prepared by shearing 1/16 inch thick sheet stock. The TiN coated samples were coated by BriCoat, Inc., Oldsmar, FL.

Figure B1 shows the apparatus used throughout the experiments. Initial tests were conducted using a 2-inch diameter quartz tube sample holder oriented with the cylinder axis horizontal. Slices 3/32 inch wide were cut ½ inch deep at right angles to the cylinder axis. The samples were placed in the slices to hold them in a vertical orientation. The sample holder was placed on a 4 inch high quartz pedestal made from the same stock as the sample holder. In this case the cylinder axis was oriented vertically. Testing at 572ºF showed severe dissolution/corrosion of the quartz. Consequently, graphite was chosen for a new pedestal and sample holder. A 2-inch outside diameter graphite cylinder, 6-inches high with ¼-inch thick walls served as a sample support and pedestal. The cylinder was cut into two 3-inch long sections to facilitate sample loading. The bottom section served as the pedestal and the other served as the sample holder. Three 3/32-inch wide saw cuts 3/8-inches deep, each 3/8-inch from its neighbor were cut across the top of the sample support for placement of the sample coupons. One TiN coated copper, one TiN coated 304 stainless steel and one Grade 7 titanium coupon consisted of the sample charge for each heating run. Each was placed in one of the saw cuts in the sample holder. This whole arrangement was placed in a 400 mL Pyrex beaker located in the center of the bomb. When the autoclave head was set in place, the bottom of the thermowell was located next to the center point of the samples. Calculations showed that approximately 90 mL of water would be in the gas space of the bomb at 572°F. Consequently, 150 mL of water was added to the beaker just prior to placing the head on the autoclave. The excess water insured that the steam would be wet throughout the test. HCl was added to water up to the 150 mL volume for the acidified tests. SO_2 was generated in situ by the action of the acid on sodium metabisulfate according the following reaction.

$$Na_2S_2O_5 + 2HCl \longrightarrow 2SO_2 + 2NaCl + H_2O$$

Carbon dioxide was added to the autoclave from a gas cylinder prior to heating. All tests were made using an initial CO_2 pressure of 50 psi.

Temperature was controlled with a Parr model 4842 PID controller equipped with an iron-constantan thermocouple. The controller controlled the temperature to +/-4°F once the operating temperature had been achieved. Overshoot during heat-up was prevented by staged heating.

This was accomplished by raising the set point in three steps. The set point was raised when the temperature had stabilized from the last raise.
Temperature was observed on a digital temperature indicator that was separate from the controller indicator and used a separate chromel-alumel thermocouple. A third thermocouple, also a chromel-alumel thermocouple, was connected to a Houston Instruments Omni Scribe Model D5000 strip chart recorder. All temperature measurements were within +/-2°F of each other.

Pressure was measured by a 2000 psi full scale mechanical gauge. Comparison of the pressure with the wet steam table pressure for the indicated temperature gave assurance that the temperature reading was correct.

Each experiment was conducted for three days duration. Then the autoclave was cooled, the gas pressure vented and the samples removed. Samples were washed to remove any soluble salts and dried and stored for SEM analysis. Liquid volumes were measured, the pH was recorded and samples of the water were saved for analysis if needed. Figures B1-4 show the components in the experimental set up. Metallographic examination of the metal coupons was conducted on a Hitachi Model HR 4307 high-resolution scanning electron microscope.

Figure B1. Experimental apparatus

Figure B2. Sample holder and beaker for holding aqueous charge

Figure B3. Sample holder with samples before a test.

Figure B4. Sample holder with samples after a test.

B4. Samples for Corrosion Testing

Test conditions were as follows:

- Temperatures of 482°F, 527°F, 572°F
- Test time of 72 hours
- The coated samples had a coating thickness of about 5µm
- The titanium samples tested were uncoated

The test schedule is shown in Table B1.

Table B1. Condensing heat exchanger materials test schedule

Series	**482°F**	**527°F**	**572°F**
1 (Control)	Air at room pressure	Air at room pressure	Air at room pressure
2 (Blank)	50 psi CO_2	50 psi CO_2	50 psi CO_2
3 (Low)	1.25 g $Na_2S_2O_5$*, 0.70 g HCl, 50 psi CO_2	1.25 g $Na_2S_2O_5$*, 0.70 g HCl, 50 psi CO_2	1.25 g $Na_2S_2O_5$*, 0.70 g HCl, 50 psi CO_2
4 (High)	6.5 g $Na_2S_2O_5$, 3.5 g HCl, 50 psi CO_2	6.5 g $Na_2S_2O_5$, 3.5 g HCl, 50 psi CO_2	6.5 g $Na_2S_2O_5$, 3.5 g HCl, 50 psi CO_2

* Sodium metabisulfite used as SO_2 source

One final test was conducted to compare commercially pure titanium with Grade 7 titanium. It was run at 572°F, 50 psi CO_2, 7.4 g HCl and 6.25 g $Na_2S_2O_5$ for 3 days. These extremes were chosen as an absolute limit to the conditions that may exist in the heat exchanger.

All tests used water to make a solution volume of 150 mL with the above reagents. Room pressure air was present in the reactor when it was pressurized to 50 psi with CO2.

B5. Results and Discussion

Test results are shown in Table B2. Final pH values for Tests 1-6, where no acid was added, were predictably high. Tests 7-15 had acid added and the final pH values were lower. The values for Tests 14 and 15 were lower yet because of the higher initial concentrations of acid added initially and little reaction with the titanium coupons versus considerable reaction with the copper and stainless steel coupons in Tests 8-13.

The TiN coated copper samples all were increasingly affected with increasing severity of conditions. Significant flaking of oxides was observed in Test 7 and continued through Test 13. There was little macro change in the surface condition of the TiN coated stainless samples until acid was added beginning in Test 7. Then the coating degraded with severity depending on the temperature and acidity. By Test 8, the oxide coating was so thick that flaking became common.

All grade 7 titanium coupons showed formation of a colored surface oxide. Very little reaction occurred after the oxide coating was formed. In Tests 14 and 15, higher acid concentration was used with no noticeable effect on the surface. Also in these tests, commercially pure titanium was tested with the grade 7 titanium. It too was relatively unaffected, although some rounding of the cut edges was observed. Further testing of the commercially pure titanium would be necessary to determine if it is stable enough under TIPS operating conditions.

Table B2. Test conditions and observations

Test No.	Conditions	Observations				
		Final pH	**Test Quality**	**TiN coated Cu**	**TiN coated 303 Stainless**	**Grade 7 Ti**
1	482°F Control	5.5	Good	Black surface	Appears unaffected	Gold surface
2	527°F Control	6.0	Good	Black surface	Appears unaffected	Gold surface
3	572°F Control	6.0	Good	Grey surface	Appears unaffected	Gold surface
4	482°F Blank	5.0	Good	Green-grey surface	Reddish surface	Gold surface
5	527°F Blank	4.8	Good	Green-red surface	Reddish-blue surface	Gold surface
6	572°F Blank	6.0	Good	Grey surface	Blueish gold surface	Gold surface
7	482°F Low	2.1	Good	Powdery copper carbonate surface	Powdery black oxide surface	Gold surface
8	527°F Low	2.3	Good	Flaky black copper oxide	Flaky black oxide	Gold-violet surface
9	572°F Low	2.4	Good	Flaky copper carbonate	Flaky black oxide	Greenish-blue surface
10	482°F High	2.0	Good	Heavy flaky black oxide	Flaky green oxide	Reddish-Blue surface
11	527°F High	1.9	Good	Heavy flaky blue-black oxide	Heavy flaky black oxide	Reddish-Blue surface
12	572°F High		Failed			
13	572°F High	1.9	Good	Heavy flaky black oxide	Heavy flaky black oxide	Blue surface
14[1]	572°F High	1.5	Good			Pure Ti: Tan surface; Grade 7Ti: Green-gold surface
15[1]	572°F Xhigh[2]	1.2	Good			Pure Ti: dk tan surface; Grade 7 Ti: Goldish-blue surface

[1] These tests were conducted with Commercially Pure and Grade 7 titanium
[2] Test conducted with twice the HCl concentration of the high level tests

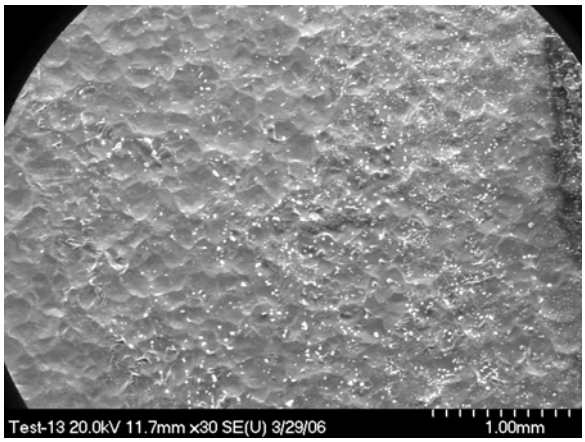


Figure B5. Grade 7 Ti with NaCl crystals on surface

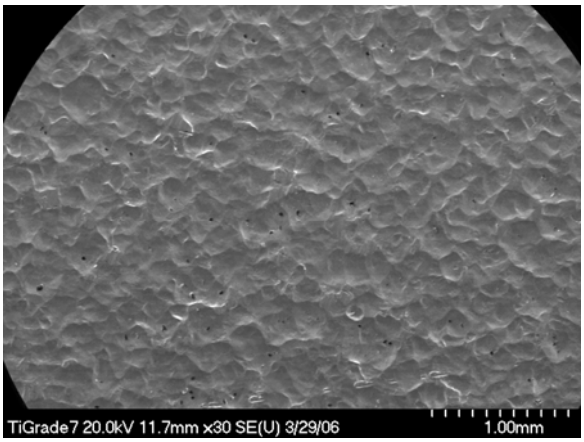


Figure B6. Clean area of Grade 7 Ti

Selected samples were chosen for examination with the scanning electron microscope. Figure B5 shows a sample of grade 7 titanium from Test 13 (572°F, 50 psi CO_2, high acid and SO_2) showing some of the small NaCl crystal decorations that were observed on it. The crystals were the result of NaCl splashing from the solution to the metal coupon and precipitation from solution. Figure B6 shows another area of the coupon that was absent the NaCl-crystals. The rumpled surface was present on the sample sheet when it arrived from the supplier. Note the lack of any pitting corrosion and the regularity of the surface undulations.

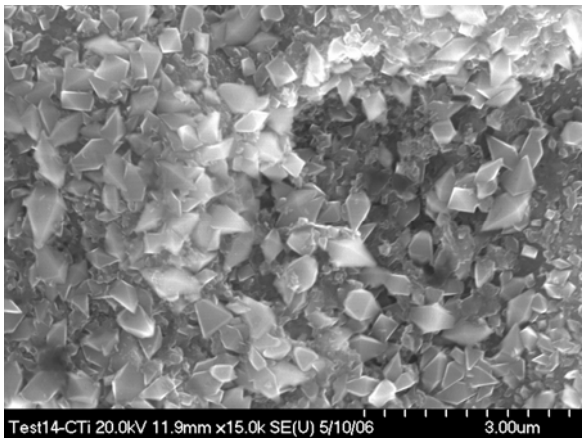


Figure B7. Commercial Ti surface showing crystals of TiO_2

Figure B7 shows a feature that was often observed on the surface of the commercially pure Ti sample from test 15 (572°F, 50 psi CO_2, extra high acid and SO_2). These are surface decorations of TiO_2 crystals indicating that some reaction had occurred. The surface oxide coating was thick enough over the entire sample coupon that TiO_2 was always observed. However, the corrosion affect was sufficiently retarded that this material should remain to be considered as a candidate for heat exchanger material. Further testing is required to determine the actual corrosion rate (in mils/yr).

Microprobe analysis of the surfaces of selected coupons was conducted to identify coatings and decorations on them. Figure B8 shows a clear region of grade 7 titanium from Test 15. The surface is unreacted titanium. The oxide coating is so thin that it was not measured by the analytical methods used.

Figure B9 shows the surface of grade 7 titanium from Test 15. Here the surface oxide is thick enough that its composition could be analyzed. However, the atomic ratio is too low for the common oxides of titanium. This indicates that some of the underlying titanium is adding to the analysis.

Figure B10 shows some of the surface decoration that was observed on the Test 15 sample. It is a complex compound containing sodium and sulfur from the atmosphere. It also contains vanadium and chromium which cannot be accounted for from the reactants added to the autoclave. There probably was some drainage of corroded 316 stainless steel fittings located in the piping connected to the autoclave head. One fitting did develop a leak part way through the testing phase of the research. The leak affected only the latter 3 experiments.

Figures B11 and B12 show the surface of the commercially pure titanium from Test 15. Figure 11 is an analysis of a broad area of uniformly smooth surface and Figure 12 is of a rough area of surface. Both areas showed titanium and oxygen as the predominant species. Figure 11 has a high Ti:O atomic ratio as was observed in the grade 7 titanium whereas Figure 12 shows a Ti:O atomic ratio of 1.87 which is close to the 2.0 that would be expected for TiO_2.

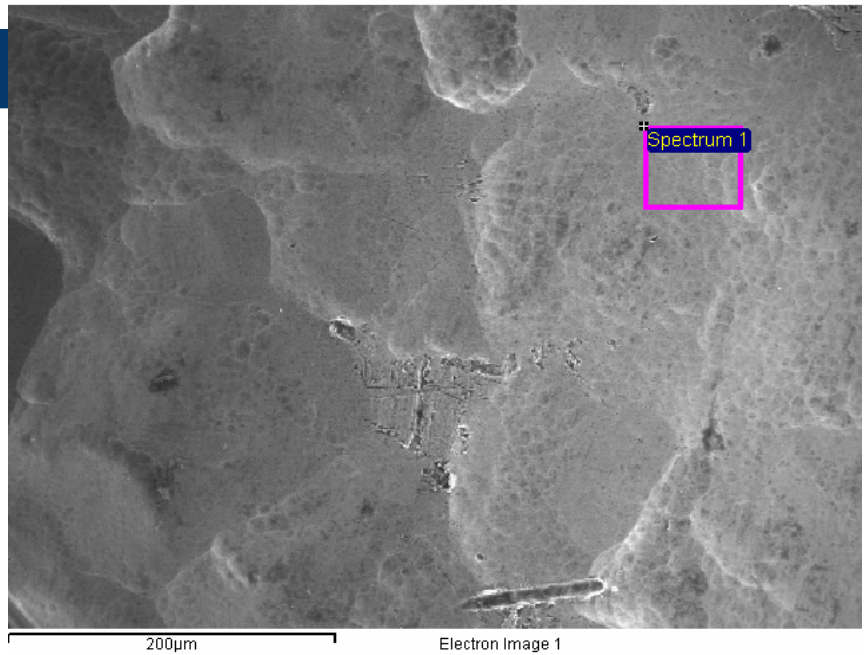
Condenser materials

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalized)
Number of iterations = 1

Standard :
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
Ti K	100.00	100.00
Totals	100.00	



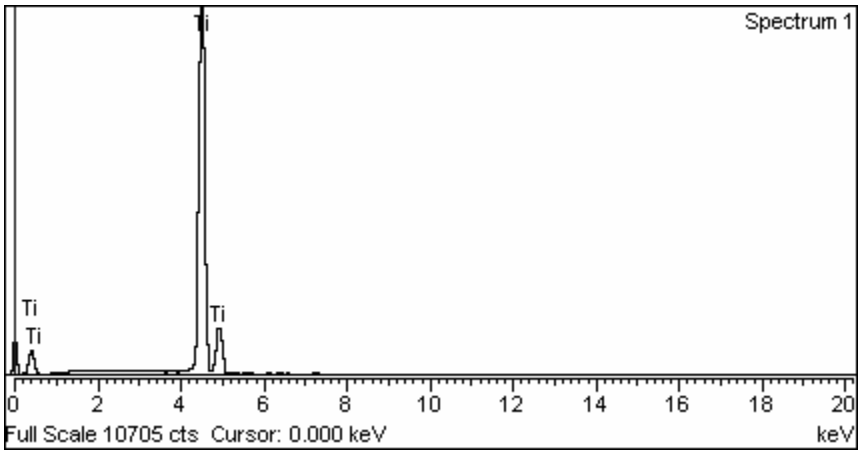


Figure B8. Ti Grade 7, Test 7

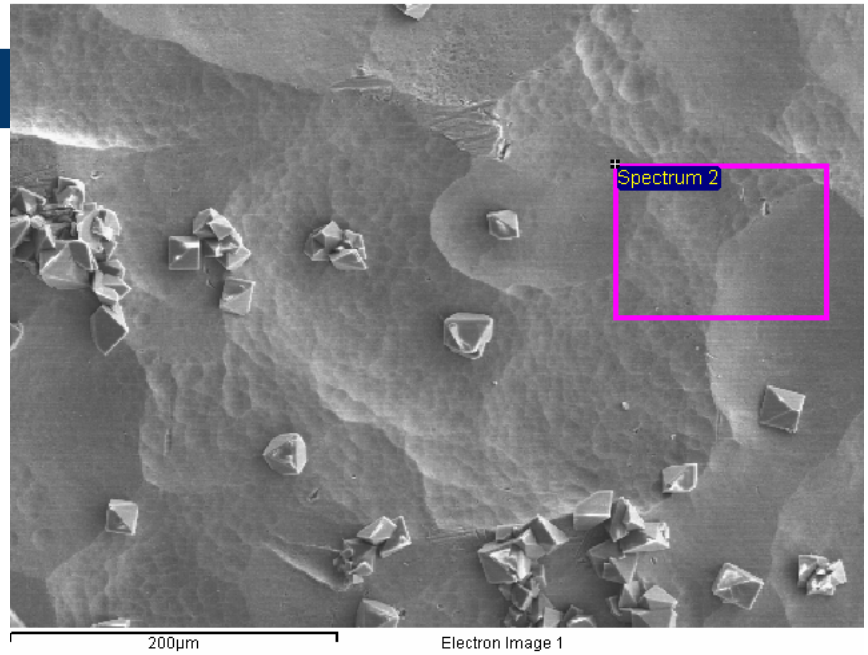
Condenser materials

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalized)
Number of iterations = 3

Standard :
O SiO2 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	21.35	44.83
Ti K	78.65	55.17
Totals	100.00	



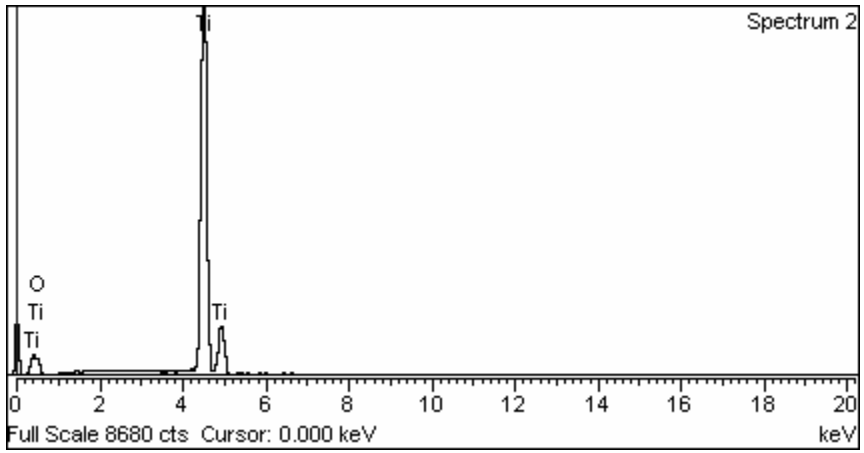


Figure B9. Grade 7 titanium, Test 15

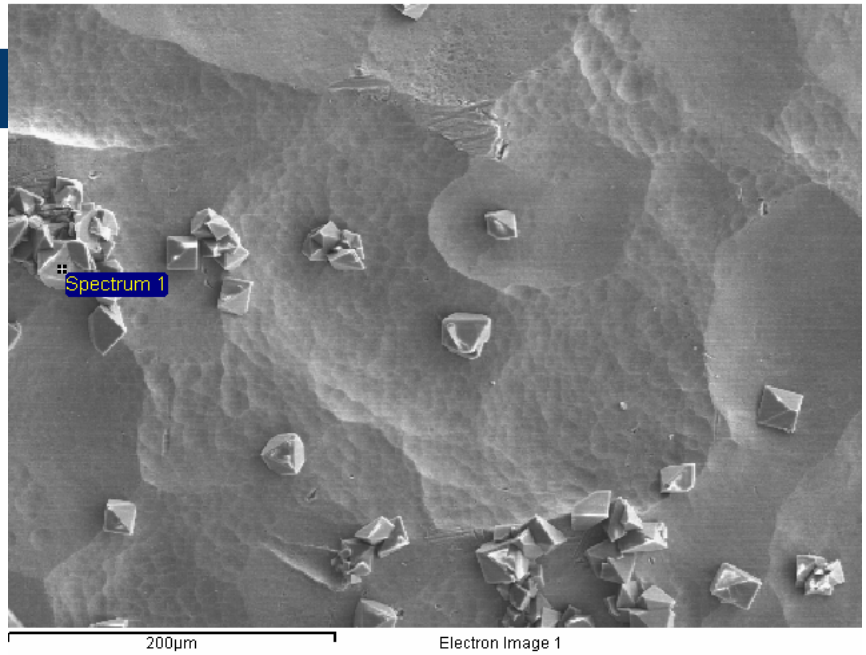
Condenser materials

Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalized)
Number of iterations = 4

Standard :
O SiO2 1-Jun-1999 12:00 AM
Na Albite 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
V V 1-Jun-1999 12:00 AM
Cr Cr 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	53.42	73.08
Na K	5.44	5.18
Al K	2.30	1.86
S K	13.09	8.94
Ti K	2.32	1.06
V K	4.21	1.81
Cr K	18.57	7.82
Fe K	0.65	0.25
Totals	100.00	



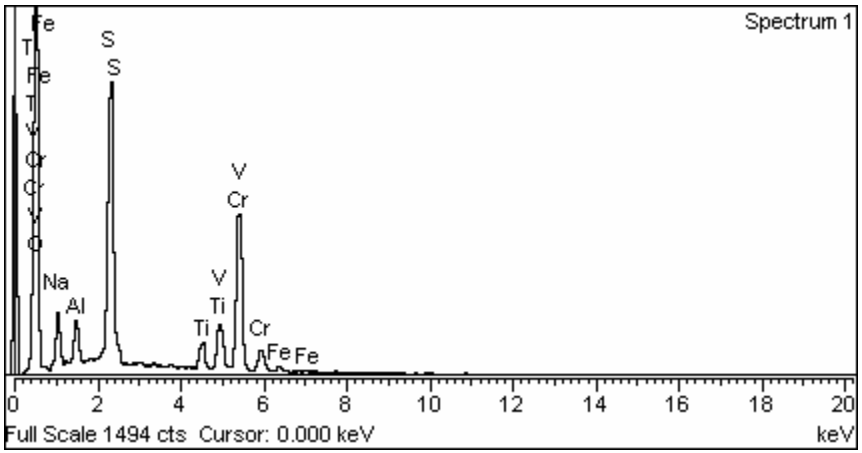


Figure B10. Grade 7 titanium, Test 15

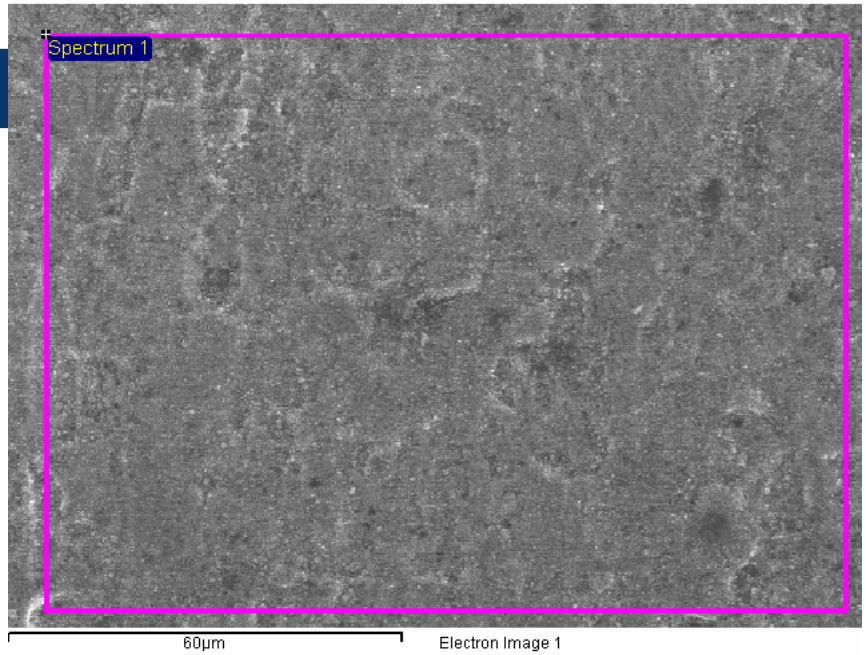
Condenser materials

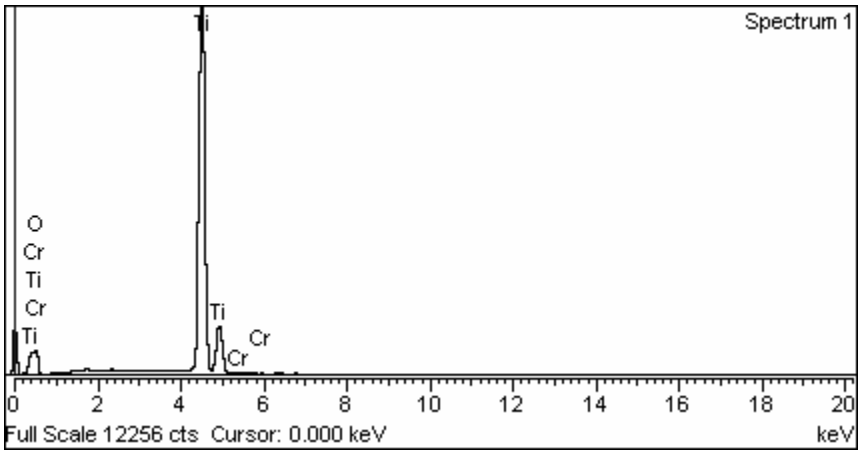
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalized)
Number of iterations = 3

Standard :
O SiO2 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Cr Cr 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	29.64	55.79
Ti K	69.89	43.94
Cr K	0.47	0.27
Totals	100.00	





FigureB11. Commercially pure titanium, Test 15

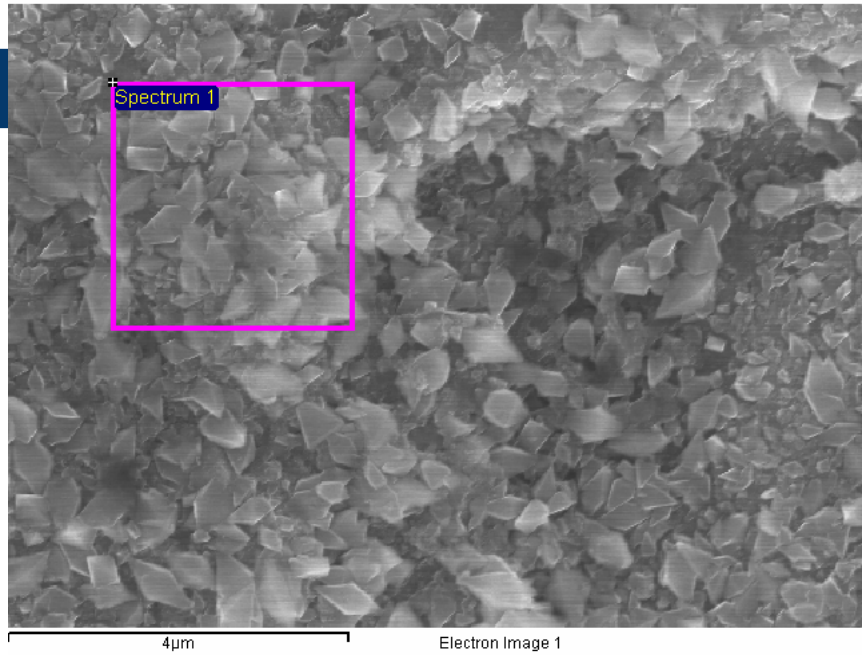
Condenser materials

Spectrum processing :
Peak possibly omitted : 1.800 keV

Processing option : All elements analyzed (Normalized)
Number of iterations = 3

Standard :
O SiO2 1-Jun-1999 12:00 AM
Ti Ti 1-Jun-1999 12:00 AM
Cr Cr 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
O K	38.16	64.90
Ti K	61.16	34.74
Cr K	0.68	0.36
Totals	100.00	



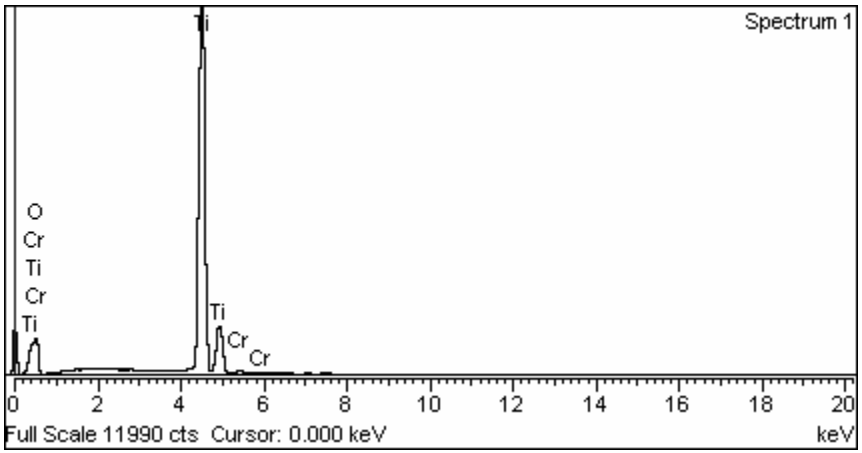


Figure B12. Commercially pure titanium, Test 15

From the results it is easy to see that the Ti was the better material because of passivation. This should be no surprise, because titanium is often selected for highly corrosive environments because of its relative inexpensive cost and the ability to form a passive, resilient oxide layer. The only uncertainty came with respect to how well it stayed attached to the surface in this extreme environment. Passivation is only successful if the layer is formed in situ (as opposed to being formed by the corrosion of the metal and redeposited as a precipitate). Oxides that are formed from the precipitation of dissolved metal will not remain adhered to the surface and therefore will not protect the metal. This explains the observed "flaky oxides" in the TiN coated samples. Copper and iron were dissolved and formed the precipitates on the surface. A classic example of this is the rusting of steel—iron oxide is formed and redeposited on the surface randomly. However, as shown in this study the TiO_2 that was observed was actually formed from the metal, and was therefore quite resilient.

This can be better explained electrochemically. Figure B13, the Pourbaix diagram for Ti, shows that TiO_2 is indeed the most prevalent species to form on Ti over the entire water stability region. In fact, the only conditions under which corrosion could take place is in an extreme reducing atmosphere. This is shown graphically in Figure B14 which shows a typical polarization curve showing the area which is protected by passivation. The lower portion of this curve for Ti would be below an Eh of -0.4 V at pH 0. Comparing the two diagrams, we see that Ti will not corrode under conditions in which water is formed. Also, based on the polariziation of Ti, the metal won't be transpassive and potentially corroded until the oxidation potential is greater than 1.2 V at pH 14! The use of titanium is perfect for this extreme condition of temeperature and pH.

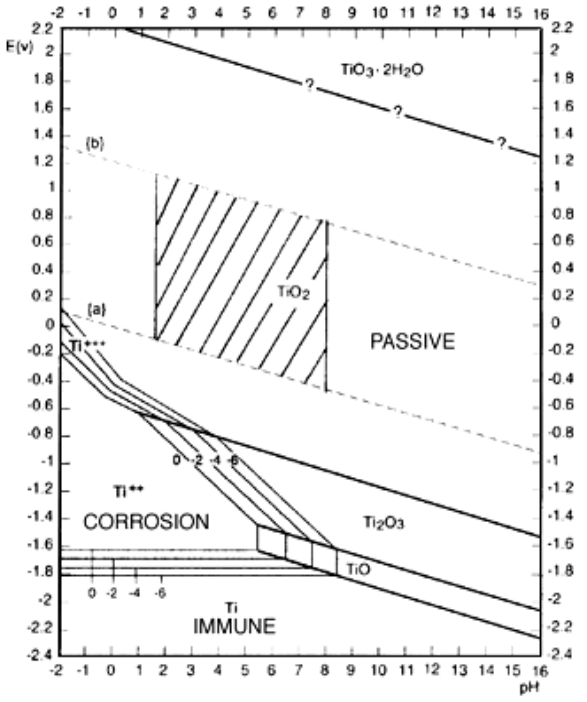


Figure B13. Pourbaix diagram for Ti-Water (9).

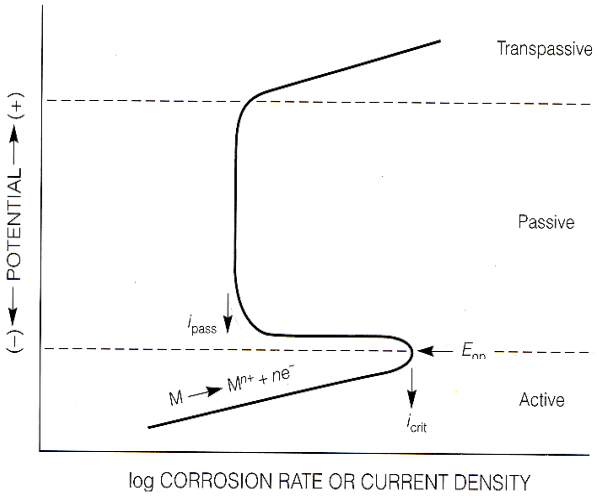


Figure B14. Typical Polarization Curve for metals (10).

B6. Conclusions

Materials for the TIPS condensing heat exchanger must be immune to chemical attack under mildly acidic conditions for temperatures as high as 482-572°F. Several coated materials as well as titanium alloys were investigated to determine their suitability for such conditions. Diamond and plasma sprayed materials were eliminated due to a lack of technology to apply them to the complicated shape of a condensing heat exchanger or to the fact that they have inherent porosity that provides a pathway for solution attack on the underlying substrate heat exchange material.

TiN and commercially pure titanium and Grade 7 titanium were deduced to show sufficient promise for laboratory testing under TIPS condensing heat exchanger conditions. Coupons of TiN coated copper or 303 stainless steel and commercially pure titanium and Grade 7 titanium were placed in an autoclave for three days per set of conditions. These conditions included the temperature range of 482-572°F, water, water plus CO_2, water plus CO_2 plus low concentrations and higher concentrations of HCl and SO_2.

Results of this testing program showed that the TiN coating samples failed under the acidic conditions, but the titanium samples—especially the Grade 7 titanium-- offered promise. No localized pitting attack was observed and little if any general attack was noticed.

Longer term tests under broader conditions (including attack on welds) are needed to ascertain the applicability of titanium or its alloys as a condensing heat exchanger material.

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